

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

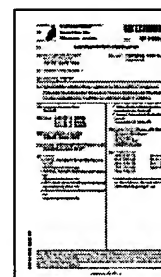
**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THOMSON  DELPHION		RESEARCH	PRODUCTS	INSIDE DELPHION
Log Out Work Files Saved Searches	My Account Products	Search: Quick/Number Boolean Advanced Derwent		

The Delphion Integrated View

Get Now:  PDF More choices...	Tools: Add to Work File: Create new Work File
View: Expand Details INPADOC Jump to: Top	Go to: Derwent  Email

- ⓘ **Title:** **EP0609888B1: Semiconductive ceramics having negative temperature coefficient of resistance**[\[German\]](#)[\[French\]](#)
- ⓘ **Derwent Title:** Semiconductive ceramics having negative temp. coefft. of resistance - enables feeding of a heavy current [\[Derwent Record\]](#)
- ⓘ **Country:** EP European Patent Office (EPO)
 ⓘ **Kind:** B1 Patent (See also: [EP0609888A1](#))
- ⓘ **Inventor:** Ishikawa, Terunobu c/o Murata Manufacturing Co Ltd;
 Nakayama, Akinori c/o Murata Manufacturing Co Ltd;
 Niimi, Hideaki c/o Murata Manufacturing Co Ltd;
 Kittaka, Toshihiko c/o Murata Manufacturing Co Ltd;
 Takagi, Hiroshi c/o Murata Manufacturing Co Ltd;
 Tomono, Kunisaburo c/o Murata Manufacturing Co Ltd;
- ⓘ **Assignee:** MURATA MANUFACTURING CO., LTD.
[News, Profiles, Stocks and More about this company](#)
- ⓘ **Published / Filed:** 1998-06-17 / 1994-02-03
- ⓘ **Application Number:** EP1994000101667
 ⓘ **IPC Code:** [C04B 35/00](#); [C04B 35/42](#); [C04B 35/50](#);
 ⓘ **ECLA Code:** [C04B35/50](#); H01C7/04C2;
- ⓘ **Priority Number:** 1993-02-05 **JP1993000018997**
 1993-02-26 **JP1993000038328**
 1993-11-04 **JP1993000275443**
- ⓘ **Abstract:** [From equivalent [EP0609888A1](#)] Semiconductive ceramics having negative temperature coefficient of resistance, which is mainly composed of an oxide of a rare earth transition element excluding Ce and including Y, with addition of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce.
- ⓘ **Attorney, Agent or Firm:** Schoppe, Fritz, Dipl.-Ing. ;
 ⓘ **INPADOC Legal Status:** [Show legal status actions](#) **Get Now:** [Family Legal Status Report](#)
 ⓘ **Designated Country:** DE FR GB
 ⓘ **Family:** [Show known family members](#) (at least 7)
- ⓘ **Description:** [Expand full description](#) [From equivalent [EP0609888A1](#)]
- + **BACKGROUND OF THE INVENTION**
 + **Field of the Invention**
 + **Description of the Background Art**



- + **SUMMARY OF THE INVENTION**
- + **BRIEF DESCRIPTION OF THE DRAWINGS**
- + **DESCRIPTION OF THE PREFERRED EMBODIMENTS**
- + **(Example 1)**
- + **(Example 2)**
- + **(Example 3)**
- + **(Example 4)**
- + **(Example 5)**
- + **(Example 6)**
- + **(Example 7)**
- + **(Example 8)**

First Claim:





[Show all claims](#)

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Si, Zr, Hf, Ta and Ce in a range of 0.001 to 5 mole percent.

[German] [French]

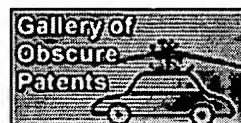
**Forward
References:**

Go to Result Set: Forward references (4)

PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6358875	2002-03-19	Kawase; Yoichi	Murata Manufacturing Co., Ltd.	Semiconductive ceramic semiconductive ceramic semiconductive ceramic
	US6090735	2000-07-18	Nakayama; Akinori	Murata Manufacturing Co., Ltd.	Semiconductive ceramic composition and semico ceramic element using th
	US6054403	2000-04-25	Kawase; Yoichi	Murata Manufacturing Co., Ltd.	Semiconductive ceramic semiconductive ceramic using the same
	US5858902	1999-01-12	Ishikawa; Terunobu	Murata Manufacturing Co., Ltd.	Semiconducting ceramic compounds having nega resistance-temperature characteristics with critic temperatures

**Other Abstract
Info:**

CHEMABS 121(20)243539D DERABS C94-250761



[Nominate this for the Gall](#)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 609 888 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
17.06.1998 Bulletin 1998/25

(51) Int Cl.⁶: **C04B 35/00**, C04B 35/42,
C04B 35/50

(21) Application number: **94101667.7**

(22) Date of filing: **03.02.1994**

(54) **Semiconductive ceramics having negative temperature coefficient of resistance**

Halbleitende Keramikmaterialien mit negativem Temperaturkoeffizienten des Widerstands

Céramique semi-conductrice à coefficient de température négatif de la résistance

(84) Designated Contracting States:
DE FR GB

(30) Priority: **05.02.1993 JP 18997/93**
26.02.1993 JP 38328/93
04.11.1993 JP 275443/93

(43) Date of publication of application:
10.08.1994 Bulletin 1994/32

(73) Proprietor: **MURATA MANUFACTURING CO., LTD.**
Nagaokakyo-shi, Kyoto 617 (JP)

(72) Inventors:
• **Ishikawa, Terunobu c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)
• **Nakayama, Akinori c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)
• **Niimi, Hideaki c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)
• **Kittaka, Toshihiko c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)

• **Takagi, Hiroshi c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)
• **Tomono, Kunisaburo c/o Murata Manufacturing Co Ltd**
Nagaokakyo-shi, Kyoto (JP)

(74) Representative: **Schoppe, Fritz, Dipl.-Ing.**
Schoppe & Zimmermann
Patentanwälte
Postfach 71 08 67
81458 München (DE)

(56) References cited:
EP-A- 0 395 400 **EP-A- 0 467 590**
EP-A- 0 623 569 **EP-A- 0 626 356**
DE-A- 2 824 408 **JP-A- 1 290 549**
JP-A- 5 612 580 **US-A- 4 013 592**
US-A- 4 062 932

• **PATENT ABSTRACTS OF JAPAN vol. 11, no. 13**
(C-397)14 January 1987 & JP-A-61 187 938
(MATSUSHITA) 21 August 1986

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 609 888 B1

Description

The present invention relates to semiconductive ceramics having negative temperature coefficient of resistance.

In general, an element for preventing an inrush current is prepared from an element (NTC element) having negative temperature coefficient of resistance, whose electric resistance value decreases with a rise in temperature. This NTC element suppresses an inrush current due to a high resistance value at the room temperature, and thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

In a switching power source, for example, an inrush current flows at the instant when a switch is turned on, and hence the so-called NTC element is employed for absorbing such an initial rush current. When the switch is turned on, therefore, the NTC element suppresses the inrush current. The NTC element thereafter increases in temperature and decreases in resistance by self heating, to reduce power consumption in a stationary state.

When a toothed wheel of a gear which is so formed that supply of lubricating oil is started upon starting of a motor is immediately rotated at a high speed by the motor, the lubricating oil is so insufficiently supplied that the toothed wheel may be damaged. When a lapping machine which is employed for grinding a surface of ceramics by rotating a grindstone is rotated at a high speed immediately upon starting of a driving motor, on the other hand, the ceramics may be cracked.

In order to solve each of the aforementioned problems, it is necessary to delay the starting of the motor for a constant period. The NTC element is employed as an element for delaying the starting of the motor in such a manner.

The NTC element reduces a terminal voltage of the motor in starting, whereby it is possible to delay the starting of the motor. Thereafter the NTC element increases in temperature and decreases in resistance by self heating, so that the motor is normally rotated in a stationary state.

The aforementioned element for preventing an inrush current or delaying motor starting is generally formed by an NTC element which is prepared from a transition metal oxide having a spinel structure.

However, the conventional NTC element has such a disadvantage that the rate of reduction in resistance (constant B) caused by a temperature rise cannot be more than 3200K. Therefore, the resistance value of the NTC element cannot be sufficiently reduced in a high-temperature state, and hence power consumption inevitably increases in a stationary state. When the NTC element is in the form of a disk, for example, the resistance value in a high-temperature can be sufficiently reduced by enlarging its diameter or making its thickness thinner. However, such a countermeasure is contradictory to requirement for miniaturization of an electronic component. Further, there are limits to thinning to satisfy the strength.

In relation to an improvement in this point, known is a multilayer NTC element which is prepared by stacking a plurality of ceramics layers with interposition of a plurality of internal electrodes and forming a pair of external electrodes on side surfaces of the laminate for alternately electrically connecting the internal electrodes with the pair of external electrodes.

However, the internal electrodes which are opposed to each other are so close to each other that the multilayer NTC element may be broken by a current exceeding several amperes.

The inventors have made various composition experiments and practical tests to deeply study materials showing negative temperature coefficient of resistance, and noted oxides of rare earth transition elements. The rare earth transition element oxides have such characteristics that B constants increase and specific resistance decrease with temperature rises. Such characteristics are described in literature (Phys. Rev. B6, [3] 1021 (1972)) by V. G. Bhide and D. S. Rajoria.

Although these rare earth transition element oxides exhibit small resistance value at a high temperature as compared with the conventional transitional metal oxides having a spinel structure, the same exhibit small B constant, with no provision of practical and meritorious effects.

US-A-4,013,592 relates to a high temperature thermistor composition which comprises a spinel-type MgAl_2O_4 and perovskite-type LaCrO_3 or $(\text{La}, \text{Sr})\text{CrO}_3$. The composition is usable for the temperature range from 400°C to 600°C. Further, a high temperature thermistor composition is disclosed which comprises spinel-type solid solution $\text{Mg}(\text{Al}, \text{Cr})_2\text{O}_4$ and perovskite-type solid solution $(\text{La}, \text{Sr})\text{CrO}_3$ or LaCrO_3 . Such a composition is usable for a higher temperature range of up to 1000°C.

EP-A-0623569 relates to a ceramic composition for a thermistor element. The composition is used for a thermistor exhibiting a stable resistance value over a wide temperature range and is capable of being used for a prolonged time. The composition is represented by the formula $(\text{M}^1\text{M}^2\text{O}_2)_{1-x} \cdot \text{M}^1\text{AlO}_3)_x$ wherein M^1 is an element selected from the elements of the group 3A excluding La and M^2 is an element of the groups 4A, 5A, 6A, 7A and 8. The composition may be YCrO_3 to which 1 weight percent SiO_2 is added.

EP-A-0626356 concerns a ceramic composition of the formula $(\text{M}^1_{1-x} \cdot \text{N}^1_x)(\text{P}^2_{1-y-x} \cdot \text{N}^2_y \cdot \text{Al}_2)\text{O}_3$ where M^1 is one or more selected from the group 3A elements of the periodic table excluding La, N^1 is one or more selected from the group 2A elements of the periodic table, P^2 is one or more selected from the elements from the groups 4A, 5A, 6A, 7A and 8 of the periodic table whose oxides exhibit p-characteristics, and N^2 is one or more selected from the elements

of the groups 4A, 5A, 6A, 7A and 8 whose oxides exhibit n-characteristics. The composition may be $Y(Cr_{0.6}Fe_{0.2}Al_{0.2})O_3$ to which SiO_2 is added.

JP-A-56125803 concerns a thermistor having a ceramic resistance body consisting of $LaCo_{1-x}V_xO_3$ in which x is 0.05-0.4. The ceramic contains an oxide of a rare earth element (La_2O_3) and oxides of transition elements (CoO and V_2O_5).

JP-A-1290549 concerns an oxide semiconductor composition for a negative temperature coefficient thermistor. This composition mainly contains an oxide of a rare earth element (La) and oxides for transition elements (Co, Mn).

It is the object of the present invention to provide semiconductive ceramics having negative temperature coefficients of resistance with low resistivity and a high B constant in a stationary state, to enable feeding of a heavy current.

This object is achieved by semiconductive ceramics according to claim 1 and claim 2.

The rare earth transition element oxide, such as $LaCoO_3$ or $SmNiO_3$, is not restricted in particular. $LaCoO_3$ exhibits such practical characteristics that its B constant extremely increases with a temperature rise, with high resistivity at the room temperature. Among rare earth elements, Ce is excluded since it is difficult to obtain an oxide with a transition metal. On the other hand, Y is included in the group of rare earth elements in the present invention since this element can attain characteristics and effects which are similar to those of the rare earth elements.

According to the present invention, 0.001 to 5 mole percent of the aforementioned additive is added to the main component.

It is possible to obtain a high B constant by adding at least 0.001 mole percent of at least one of Si, Zr, Hf, Ta, Sn, Sb, W, Mo, Te and Ce to the main component of a rare earth transition element oxide, since the resistance value at a room temperature can be increased with maintaining low resistance value at a high temperature. If the content of the additive exceeds 10 mole percent, however, the B constant at a high temperature is reduced below that of an NTC element which is composed of a transition metal oxide having a spinel structure. The content of the additive is set in a range of 0.001 to 5 mole percent.

As to the rare earth transition element oxide, the mole ratio of the rare earth element to the transition element is not restricted to 1:1 but may be varied. Even if the mole ratio is varied within a range of 0.6 to 1.1, it is possible to obtain a B constant which is substantially identical to that obtained at the mole ratio of 1:1. If the mole ratio is less than 0.6 or in excess of 1.1, however, power consumption in a stationary state so increases that the semiconductive ceramics cannot be applied to a circuit which is supplied with a heavy current, since the resistance value will not decrease upon a temperature rise.

As hereinabove described, the inventive semiconductive ceramics having negative temperature coefficient of resistance is composed of a rare earth transition element oxide with addition of a prescribed element, whereby it is possible to obtain an element having a high B constant at a high temperature, since the resistance value at room temperature can be increased with maintaining low resistance value at a high temperature. Therefore, it is possible to sufficiently reduce the resistance value in a temperature rise state for reducing power consumption in a stationary state, so that the element can be applied to a circuit which is supplied with a heavy current.

Thus, the semiconductive ceramics according to the present invention is applicable to an NTC element for preventing an inrush current in a switching power source which is supplied with a heavy current, or that for delaying motor starting.

While the semiconductive ceramics having negative temperature coefficient of resistance according to the present invention is applied to an element for preventing a rush current or that for delaying motor starting, the present invention is not restricted to such application.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

Fig. 1 is a characteristic diagram showing results of a test which was made by series-connecting an NTC element to a switching power source and measuring time change of a switching power source current upon power supply at a temperature of 25°C; and

Fig. 2 is a characteristic diagram showing relation between the number of times of a repetitive energization test and resistance values at a temperature of 25°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(Example 1)

This Example was carried out on a rare earth transition element oxide of $LaCoO_3$.

First, $LaCoO_3$ powder materials were prepared in the following manner: Respective powder materials of Co_3O_4 and La_2O_3 were weighed so that La was at a mole ratio of 0.95 to Co. Prescribed amounts of additives shown in Tables

1, 2 and 3 were added to the powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours. Referring to Table 1, asterisked (*) amounts are out of the scope of the present invention.

Thus obtained calcined powder materials were pulverized by jet mills. Binders were added to the powder materials, which in turn were again wet-blended for 5 hours in ball mills employing nylon balls, filtered, dried and thereafter pressure-molded into the form of disks. The disks were fired in the atmosphere at 1400°C for 2 hours, to obtain sintered bodies. Both major surfaces of the sintered bodies were coated with platinum paste by screen printing, and baked at 1000°C for 2 hours, to be provided with electrodes. NTC elements were thus obtained.

The NTC elements were subjected to measurement of electric characteristics of specific resistance values and B constants. Tables 1 to 3 as well as Tables 4 to 9 described later show resistivity values which were measured at a temperature of 25°C. Assuming that $\rho(T)$ and $\rho(T_0)$ represent resistivity values at temperatures T and T_0 respectively and \ln represents a natural logarithm, each B constant, which is a constant showing resistance change caused by temperature change, is defined as follows:

$$B(T) = [\ln \rho(T_0) - \ln \rho(T)] / (1/T_0 - 1/T)$$

Temperature change caused by the temperature increases with this value.

Referring to Tables 1, 2 and 3, the B constants at -10°C and 140°C are defined as follows:

$$B \text{ constant } (-10^\circ\text{C}) = [\ln \rho(-10^\circ\text{C}) - \ln \rho(25^\circ\text{C})] / [1/(-10 + 273.15) - 1/(25 + 273.5)]$$

$$B \text{ constant } (140^\circ\text{C}) = [\ln \rho(25^\circ\text{C}) - \ln \rho(140^\circ\text{C})] / [1/(25 + 273.15) - 1/(140 + 273.5)]$$

Figs. 1 and 2 show results of a repetitive energization test which was made on a sample according to Example 1, containing 1 mole percent of Zr. Fig. 1 shows the results of the test which was made by series-connecting an NTC element to a switching power source and measuring the time change of the switching power source current upon power supply at a temperature of 25°C. Fig. 2 is a characteristic diagram showing relation between the number of times of the repetitive energization test and resistance values at a temperature of 25°C. In this repetitive energization test, the NTC element was energized with a current for 1 minute and thereafter the power source was turned off for 30 minutes to cool the element to 25°C every cycle. As clearly understood from Figs. 1 and 2, no characteristic change was recognized even after 10000 cycles. Further, no NTC element was broken when currents of 200 A were continuously applied to 100 NTC elements. Thus, it was confirmed that the inventive NTC element is applicable to a heavy current.

Table 1

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-1	Zr	0 *	4.9	520	1590
1-2	Zr	0.000*	8.4	890	2510
1-3	Zr	0.001	11.1	1220	3020
1-4	Zr	0.01	14.8	1650	3780
1-5	Zr	0.1	18.7	2150	4480
1-6	Zr	1	19.8	2620	4730
1-7	Zr	10*	13.6	1600	3290
1-8	Zr	20*	4.7	790	1790

Table 2

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-9	Si	0.05	17.4	2010	4290

Table 2 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-10	Mo	0.05	16.7	1820	4580
1-11	Sn	0.5	20.5	2400	4680
1-12	Sb	1	17.3	1970	4450
1-13	Te	1	20.2	2630	4530
1-14	Hf	5	18.4	2260	4310
1-15	Ta	5	17.5	2100	4570
1-16	W	10*	16.4	1990	4320
1-17	Ce	10*	17.0	2090	4480

Table 3

No.	Additional Element :	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
1-18	Zr	0.05	19.6	2280	4230
	Mo	0.05			
1-19	Zr	1	18.3	2570	4550
	Sn	0.5			
1-20	Zr	0.05	17.8	2130	4510
	Sn	0.05			
	W	0.05			
1-21	Zr	1	16.2	2460	4290
	Mo	0.5			
	Ce	0.5			

(Example 2)

This Example was carried out on a rare earth transition element oxide of SmNiO_3 .

First, SmNiO_3 powder materials were prepared in the following manner: Respective powdery materials of Sm_2O_3 and NiO were weighed so that Sm was at a mole ratio of 0.95 to Ni. Additives shown in Table 4 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 4 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 4

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (K)	B Constant (-10°C) (140°C) (K)
3-1	Zr	0.05	14.8	2240	3920
3-2	Mo	0.05	14.0	2340	3870
3-3	Sb	1	13.8	2290	3790
3-4	Hf	1	12.1	2150	3740

Table 4 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (K)	B Constant (-10°C) (140°C) (K)
3-5	Ta	0.5	14.3	2230	3800
3-6	W	0.5	15.0	2090	3750
3-7	Sb	0.5	12.9	2410	3930
	Ce	0.5			
3-8	Zr	0.05	14.3	2060	3620
	Ta	0.05			
3-9	Sn	1	12.0	2220	3890
	W	1			
3-10	Si	0.1	13.7	2390	3990
	Mo	0.1			
	W	0.1			

(Example 3)

This Example was carried out on a rare earth transition element oxide of NdNiO_3 .

First, NdNiO_3 powder materials were prepared in the following manner: Respective powder materials of Nd_2O_3 and NiO were weighed so that Nd was at a mole ratio of 0.95 to Ni. Additives shown in Table 5 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 5 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

Table 5

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
4-1	Si	0.5	24.3	2030	3860
4-2	Zr	0.5	24.0	2170	3790
4-3	Mo	5	25.8	2100	3910
4-4	Sn	5	24.1	2090	3730
4-5	Sb	1	23.6	2160	3850
4-6	Ce	1	22.6	2240	3930
4-7	Si	1	25.9	2120	3710
	Sn	1			
4-8	Zr	0.5	25.4	1990	3790
	W	0.5			
4-9	Mo	0.5	24.3	1970	3860
	Ta	0.5			
4-10	Zr	0.1	24.6	2080	3900
	Sn	0.1			
	Ta	0.1			

(Example 4)

This Example was carried out on a rare earth transition element oxide of PrNiO_3 .

First, PrNiO_3 powder materials were prepared in the following manner: Respective powder materials of Pr_6P_{11} and NiO were weighed so that Pr was at a mole ratio of 0.95 to Ni. Additives shown in Table 6 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 6 also shows results of respective electric characteristics of the obtained NTC elements, which were measured similarly to Example 1.

Table 6

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\text{-cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
5-1	Zr	1	10.6	1960	3650
5-2	Mo	1	9.8	2100	3590
5-3	Sb	0.5	11.6	2060	3710
5-4	Te	0.5	8.9	1980	3690
5-5	Ta	0.05	10.3	2030	3740
5-6	W	0.05	12.0	2210	3820
5-7	Zr	1	9.7	2120	3640
	Hf	1			
5-8	Zr	0.5	9.6	1990	3630
	W	0.1			
5-9	Mo	0.1	11.3	1970	3670
	Sb	0.1			
5-10	Sb	0.5	10.2	2090	3710
	Hf	0.5			
	W	0.5			

(Example 5)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Nd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Table 7 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 7 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 7

No.	Additional Element	Content (mol%)	Resistivity ($\Omega\text{-cm}$)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-1	Zr	0.5	26.1	1870	3630
6-2	Sb	1	25.7	1720	3690
6-3	W	5	26.4	1910	3590

Table 7 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
6-4	Si	1	24.0	1860	3540
	Hf	1			
6-5	Zr	0.5	25.6	1790	3680
	Mo	0.5			
	Ta	0.5			

(Example 6)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.

First, respective powder materials of La_2O_3 , Gd_2O_3 and Co_3O_4 were weighed to obtain $\text{La}_{0.2}\text{Gd}_{0.1}\text{CoO}_3$ semiconductive ceramic materials. Additives shown in Table 8 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 8 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 8

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
7-1	Sn	0.01	22.0	2010	3750
7-2	Ta	0.5	21.9	1960	3710
7-3	Ce	1	23.7	1840	3860
7-4	Zr	0.1	22.4	2020	3650
	Mo	0.1			
7-5	Zr	0.5	23.7	1970	3700
	Te	0.5			
	Hf	0.5			

(Example 7)

This Example was carried out on a rare earth transition element oxide of $\text{La}_{0.99}\text{Y}_{0.01}\text{NiO}_3$.

First, respective powder materials of La_2O_3 , Y_2O_3 and MnO were weighed to obtain $\text{La}_{0.99}\text{Y}_{0.1}\text{NiO}_3$ semiconductive ceramic materials. Additives shown in Table 9 were added to the weighed powder materials, which in turn were wet-blended for 16 hours in ball mills employing nylon balls. Thereafter the powder materials were dehydrated, dried and calcined at 1000°C for 2 hours.

Then, the calcined powder materials were treated similarly to Example 1, to obtain NTC elements.

Table 9 also shows results of respective electric characteristics of thus obtained NTC elements, which were measured similarly to Example 1.

Table 9

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-1	Sn	5	20.6	2190	3970
8-2	Mo	1	21.5	2290	3860
8-3	W	0.5	19.7	2200	3900

Table 9 (continued)

No.	Additional Element	Content (mol%)	Resistivity (Ω -cm)	B Constant (-10°C) (K)	B Constant (140°C) (K)
8-4	Sb	0.5	20.1	2260	3840
	Ta	0.5			
8-5	Zr	1	20.6	2270	3820
	Sb	1			
	Mo	1			

Although the aforementioned Examples were carried out on oxides of LaCoO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 respectively, the present invention is also applicable to other rare earth transition element oxides, to attain similar effects.

Claims

1. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Si, Zr, Hf, Ta and Ce in a range of 0.001 to 5 mole percent.
2. Semiconductive ceramics having negative temperature coefficient of resistance, being mainly composed of an oxide which contains as main ingredients a rare earth material of the group IIIa excluding Ce and including Y and a transition element excluding Cr, with addition of at least one of Sn, Sb, W, Mo or Te in a range of 0.001 to 5 mole percent.
3. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein said oxide is at least one selected from LaCoO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 and PrNiO_3 .
4. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, wherein 0.1 to 5 mole percent of said additive is added to said main component.
5. Semiconductive ceramics having negative temperature coefficient resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Nd}_{0.1}\text{CoO}_3$.
6. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.9}\text{Gd}_{0.1}\text{CoO}_3$.
7. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 3, wherein said oxide of LaCoO_3 is $\text{La}_{0.99}\text{Y}_{0.01}\text{CoO}_3$.
8. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, being applied to an element for preventing a rush current.
9. Semiconductive ceramics having negative temperature coefficient of resistance in accordance with claim 1 or 2, being applied to an element for delaying motor starting.

Patentansprüche

1. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten, die hauptsächlich aus einem Oxid besteht, das als Hauptbestandteile ein seltenes Erdmaterial der Gruppe IIIa, ausschließlich Ce und einschließlich Y, und ein Übergangselement, ausschließlich Cr, enthält, mit einem Zusatz von zumindest einem der Elemente Si, Zr, Hf, Ta und Ce in einem Bereich von 0,001 bis 5 Mol-Prozent.

2. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten, die hauptsächlich aus einem Oxid besteht, das als Hauptbestandteile ein seltenes Erdelement der Gruppe IIIa, ausschließlich Ce und einschließlich Y, und ein Übergangselement, ausschließlich Cr, enthält, mit einem Zusatz von zumindest einem der Elemente Sn, Sb, W, Mo oder Te in einem Bereich von 0,01 bis 5 Mol-Prozent.
3. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 1 oder 2, bei der das Oxid ein Oxid ist, das aus LaCoO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 und PrNiO_3 ausgewählt ist.
4. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 1 oder 2, bei der der Hauptkomponente 0,1 bis 5 Mol-Prozent des Zusatzstoffes zugesetzt sind.
5. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 3, bei der das Oxid aus LaCoO_3 $\text{La}_{0,9}\text{Nd}_{0,1}\text{CoO}_3$ ist.
6. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 3, bei der das Oxid aus LaCoO_3 $\text{La}_{0,9}\text{Gd}_{0,1}\text{CoO}_3$ ist.
7. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 3, bei der das Oxid aus LaCoO_3 $\text{La}_{0,99}\text{Y}_{0,01}\text{CoO}_3$ ist.
8. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 1 oder 2, das für ein Element zum Verhindern eines Stromstoßes verwendet ist.
9. Halbleitende Keramik mit einem negativen Widerstandstemperaturkoeffizienten gemäß Anspruch 1 oder 2, die als ein Element zum Verzögern eines Motorstartens verwendet ist.

Revendications

1. Céramique semi-conductrice à coefficient de résistance à la température négatif, composé principalement d'un oxyde qui contient, comme ingrédients principaux, un matériau des terres rares du groupe IIIa, à l'exclusion de Ce et incluant Y, et un élément de transition, à l'exclusion de Cr, avec addition d'au moins l'un parmi Si, Zr, Hf, Ta et Ce dans une plage de 0,001 à 5 pour cent en molécules-gramme.
2. Céramique semi-conductrice à coefficient de résistance à la température négatif, composé principalement d'un oxyde qui contient, comme ingrédients principaux, un matériau des terres rares du groupe IIIa, à l'exclusion de Ce et incluant Y, et un élément de transition, à l'exclusion de Cr, avec addition d'au moins l'un parmi Sn, Sb, W, Mo ou Te dans une plage de 0,001 à 5 pour cent en molécules-gramme.
3. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 1 ou 2, dans laquelle ledit oxyde est au moins l'un choisi parmi LaCoO_3 , LaMnO_3 , SmNiO_3 , NdNiO_3 et PrNiO_3 .
4. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 1 ou 2, dans laquelle il est ajouté audit composant principal de 0,1 à 5 pour cent en molécules-gramme dudit adjuvant.
5. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 3, dans laquelle ledit oxyde LaCoO_3 est $\text{La}_{0,9}\text{Nd}_{0,1}\text{CoO}_3$.
6. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 3, dans laquelle ledit oxyde LaCoO_3 est $\text{La}_{0,9}\text{Gd}_{0,1}\text{CoO}_3$.
7. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 3, dans laquelle ledit oxyde LaCoO_3 est $\text{La}_{0,99}\text{Y}_{0,01}\text{CoO}_3$.
8. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 1 ou 2, appliquée à un élément destiné à empêcher un courant violent.
9. Céramique semi-conductrice à coefficient de résistance à la température négatif suivant la revendication 1 ou 2,

EP 0 609 888 B1

appliquée à un élément destiné à retarder le démarrage d'un moteur.

5

10

15

20

25

30

35

40

45

50

55

FIG. 1

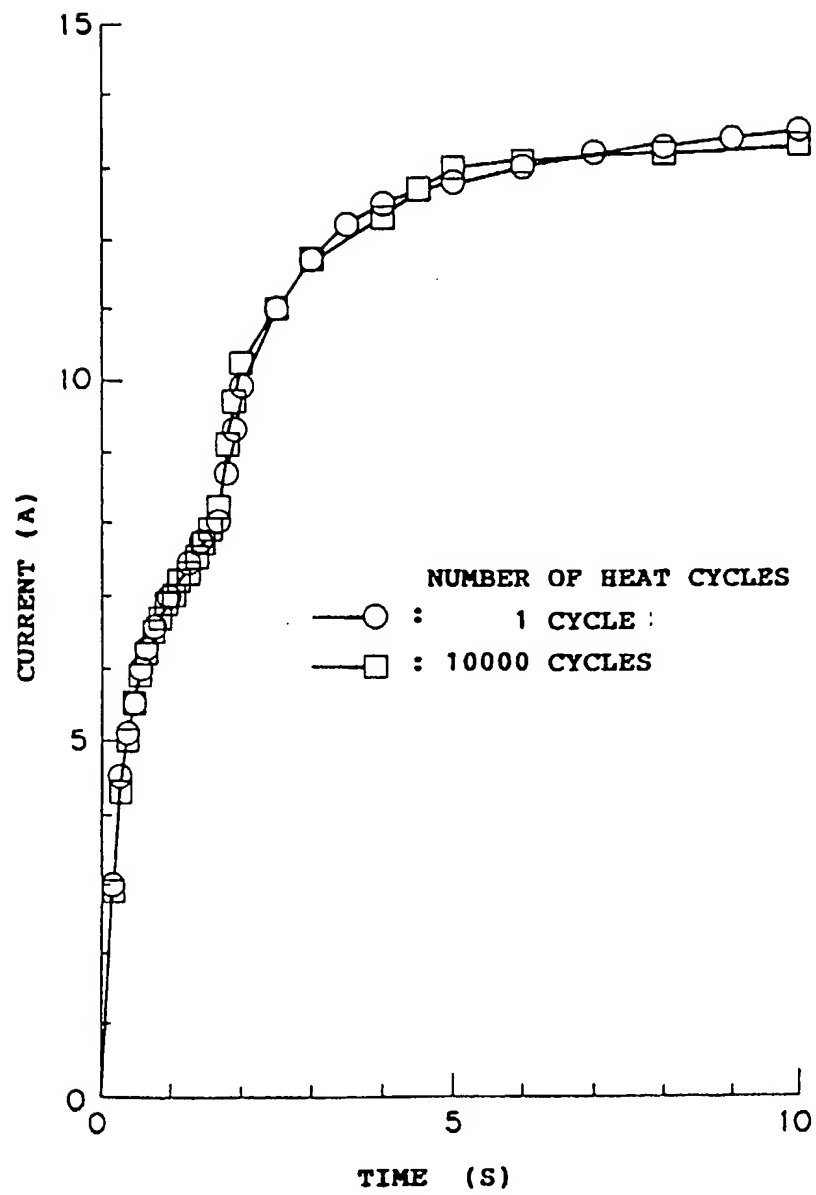


FIG. 2

